PYRITE REMOVAL FROM OIL-SHALE CONCENTRATES USING LITHIUM ALUMINUM HYDRIDE

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A new technique has been developed by the Federal Bureau of Mines for removing pyrite from oil-shale concentrates. This was accomplished by treating concentrates with a tetrahydrofuran solution of lithium aluminum hydride at reflux temperature and extracting the resulting soluble sulfide with dilute acid. By this procedure, the pyrite content of a carbonate free oil-shale concentrate was reduced from 5.0 to 0.02 percent, without objectionable alteration of the organic material (kerogen) as indicated by elemental and infrared analyses. Concentrates obtained by this method will be useful in kerogen structural studies.

According to Bradley (1), oil shale of the Green River formation was deposited in shallow, fresh-water lakes during the Eocene period. The kerogen probably formed from microscopic algae and other aquatic organisms; the minerals formed from water-soluble salts and from deposition of stream-carried silt. A typical Green River oil shale contains more than 50 percent mineral, which includes carbonates, quartz, feldspar, illite clay, and pyrite. Pyrite forms in an alkaline and reducing medium and according to Rosenthal (3), may be formed in nature under similar conditions. It is desirable to remove most or all of the minerals from oil shale in order to have a suitable sample for structural study. Ordinary concentration techniques remove other minerals but concentrate pyrite with the kerogen. This presents a special problem.

Pyrite enters into many of the reactions of kerogen, and many physical-property measurements of kerogen cannot be made when pyrite is present. For example, pyrite enters into reduction, oxidation, and hydrolysis reactions; complicates functional group analysis; and causes high background and poor resolution in X-ray diffraction analyses. Organic sulfur analyses necessitate pyritic sulfur corrections.

Previously, quantitative removal of pyrite has not been possible without objectionable alteration to the kerogen. Nitric acid completely oxidizes the pyrite, but oxidizes and nitrates the kerogen. Nascent hydrogen does not entirely remove the pyrite (2). Pyrite can be oxidized by other reagents (5), but if they were used on oil shale, drastic alteration of the kerogen probably would result.

Lithium aluminum hydride treatment quantitatively removes pyrite from oil-shale concentrates. This treatment is rapid and simple, and causes predictable changes to the kerogen.

EXPERIMENTAL PROCEDURE

Sample Preparation. Two concentrates were used in this study and were prepared from the same raw shale. The first of these, designated as acid concentrate, was prepared in the following manner: A sample of Green River oil shale was ground to pass a 100-mesh screen and treated with one normal hydrochloric acid until free of carbonate minerals. The mixture then was filtered and the residue washed with boiling water until the filtrate was neutral. The concentrate then was dried under vacuum at 60° C. for 12 hours.

The second concentrate, designated as attrited concentrate, was prepared (4) from the acid concentrate by the following procedure: Cetane was mixed with the sample to make a paste which was ground in a ball mill with an excess of water until a minimum ash was attained for the organic concentrate. The cetane then was extracted from the paste with benzene and the organic concentrate was dried under vacuum at 60° C. for 12 hours. The silicate minerals were removed by this concentration procedure, because they are preferentially wet by water.

A sample of an Illinois bituminous coal was ground to pass a 100-mesh screen and dried under vacuum at 60° C. for 12 hours.

Lithium Aluminum Hydride Treatment. Two-hundred grams of attrited concentrate and 40 grams of lithium aluminum hydride (LAH) were placed in a 3-liter flask, equipped with a reflux condenser to which a Caroxite drying tube was attached. One and one-half liters of tetrahydrofuran was slowly introduced. The reaction mixture was refluxed for one-half hour, cooled to room temperature, and vacuum filtered. The filtration was stopped while the residue was still wet. To destroy the unreacted LAH, the residue was transferred in small portions as rapidly as possible to a 4-liter beaker containing 1 liter of water. This mixture was acidified with 100 milliliters of 1 N hydrochloric acid, heated to boiling, and filtered. This acid treatment was repeated four times to insure complete removal of aluminum ions, as shown by testing the washings with ammonium hydroxide. The residue was washed with boiling water to remove the hydrochloric acid and then dried under vacuum at 60° C. for 12 hours.

The acid concentrate and the bituminous coal were treated using a similar procedure, except that 20-gram samples with 4 grams of LAH were used.

Nitric Acid Treatment. Pyrite was removed from the attrited concentrate by boiling the sample for one-half hour in 2 N nitric acid and filtering and leaching with boiling water until the filtrate was neutral. The product was dried under vacuum at 60° C. for 12 hours.

Sample Analyses. Pyrite content was determined by the modified Mott method (6). Qualitative evidence for the presence of pyrite was obtained from X-ray diffraction spectra using its 33° 2 theta peak. Ash content was determined at 1000° C. Elemental analyses were determined using the following methods: Carbon and hydrogen by combustion, nitrogen by Kjeldahl, total sulfur by Eschka, organic sulfur by subtraction of pyritic from total sulfur, oxygen by difference, and chlorine by Schoninger. Organic elemental composition was calculated on a mineral and chlorine free basis.

Infrared spectra were obtained using the potassium bromide pellet technique.

RESULTS AND DISCUSSION

Pyrite Removal. Pyrite is quantitatively removed from the oil-shale concentrates. Lithium aluminum hydride treatment lowers the pyrite content of the attrited concentrate from 5.3 percent to 0.02 percent and the pyrite in the acid concentrate from 3.1 to 0.02 percent as shown in Table 1. Further evidence of

Table 1. - Decrease of pyrite and ash content due to LAH treatment

	Attrited Concentrate		Acid Concentrate		Bituminous Coal	
	Untreated	Treated	Untreated	Treated	Untreated	Treated
Pyrite, wt. %	5.3	0.02	3.1	0.02	1.8	0.2
Ash, wt. %	8.8	5.5	44.5	43.0	9.4	6.7
Pyrite, X-ray Peak Heights	16	0	4	0	6	0

pyrite removal is shown by disappearance of the X-ray diffraction pyrite peak in the LAH treated concentrates. Pyrite removal is also reflected by decrease of the ash in the attrited concentrate from 8.8 to 5.5 percent and in the acid concentrate from 44.5 to 43.0 percent. This ash reduction approximates the amount expected due to pyrite removal.

This method, which was developed for oil shale, reduced the pyrite content of the bituminous coal sample from 1.8 to 0.2 percent.

Effect on Kerogen. Examination of available data shows little change in the kerogen structure by LAH treatment. Organic elemental analyses (Table 2) reveal

Table 2. - Organic composition of various samples

	Attrited Concentrate		HNO_3 Concentrate	Acid Concentrate		Bituminous Coal	
	Untreated	Treated		Untreated	Treated	Untreated	Treated
			WT. % 1/				
H	10.2	10.9	9.0	10.2	10.8	5.7	5.7
C	77.5	79.9	70.1	77.5	78.6	77.6	78.0
N	2.6	2.7	4.3	2.5	2.6	1.4	1.4
S	1.4	1.5	1.0	1.3	1.5	2.7	3.2
O 2/	8.3	5.0	15.6	8.5	6.5	12.6	11.7
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0
			ATOMIC RATIOS				
H/C	1.58	1.63	1.54	1.58	1.65	0.88	0.88
N/C	0.03	0.03	0.05	0.03	0.03	0.02	0.02
S/C	0.005	0.006	0.005	0.006	0.007	0.01	0.02
O/C	0.08	0.05	0.17	0.08	0.06	0.12	0.11

1/ Based on mineral and chlorine-free sample
2/ By difference

no significant differences, except for oxygen, between treated and untreated samples. The elemental analyses indicate a loss of 3.3 percent oxygen for the attrited concentrate and 2.0 percent for the acid treated concentrate. The atomic ratios of hydrogen to carbon, nitrogen to carbon, and sulfur to carbon for the LAH treated sample are approximately the same as the untreated concentrates. However, the oxygen to carbon ratios of the treated concentrates are lowered from 0.08 to approximately 0.05.

The overall infrared spectra (Figure 1) are much the same for the treated and untreated samples. Infrared spectra, however, show elimination of the 5.9 micron band which is attributed to carbonyl groups. The change noted in the 9 to 10 micron region presumably is due to better resolution of the silicate mineral bands. The carbonyl elimination and oxygen decrease may be explained by the reduction of a carboxyl group or an ester linkage to form alcohols.

Nitric acid treatment of the attrited concentrate for pyrite removal increases the nitrogen content from 2.6 to 4.3 percent and oxygen from 8.3 to 15.6 percent.

CONCLUSIONS

Pyrite has been quantitatively removed from concentrates by using lithium aluminum hydride.

The concentrate produced by LAH treatment is well suited for kerogen structural studies because the LAH reacts only with specific functional groups. Of the functional groups present in kerogen, LAH reduces carbonyl oxygen but does not attack other groups such as ethers, alkenes and amines. Since such changes can be evaluated, they do not interfere with structural studies. Hence, the lithium aluminum hydride method for the removal of pyrite is preferable to the use of strong oxidizing agents, such as nitric acid, which cause non-specific changes in the kerogen.

Since LAH treatment eliminates the pyrite from kerogen concentrates, further treatment with dilute hydrofluoric acid should produce a near mineral-free sample, which would be valuable for future studies on kerogen structure.

ACKNOWLEDGMENT

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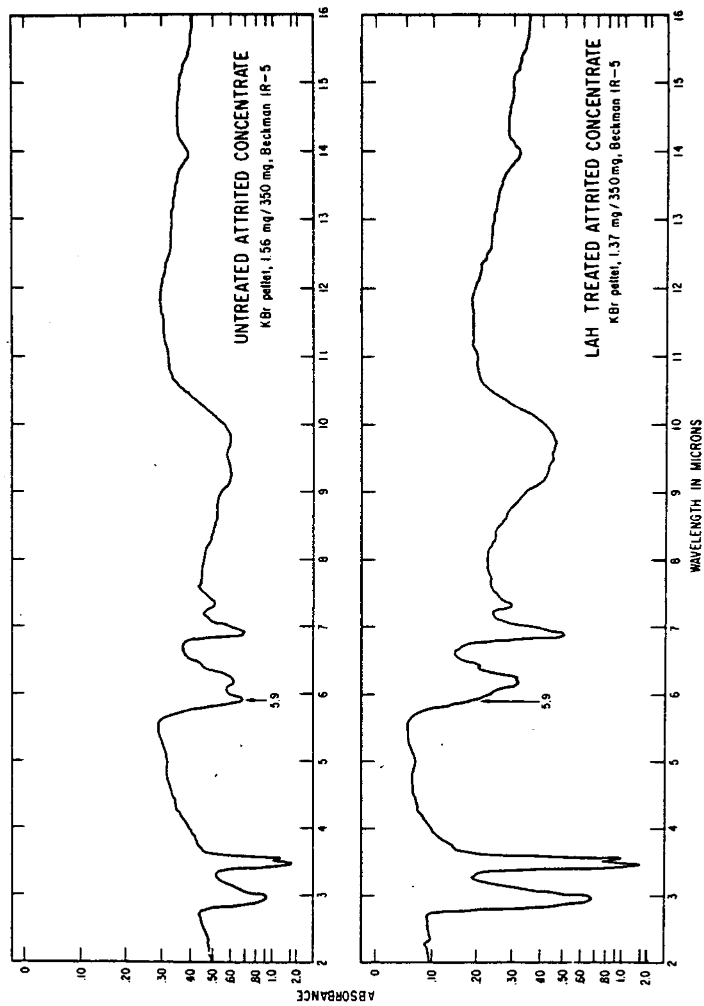

FIGURE 1.-INFRARED SPECTRA OF CONCENTRATES.

SOA-334 P

Fundamental Properties of Green River Oil Shale as Determined from Nitrogen Adsorption and Desorption Isotherms

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Oil shale, a major potential source of liquid fuels, consists of a complex mixture of organic and inorganic constituents in variable proportions. Understanding of its fundamental properties and structure may aid in improving existing methods for converting the organic matter to useful liquid and gaseous products and in devising new methods (7,8,9,10,12).

A previous publication (14) presented data on particle size, particle-size distribution, and particle-size classification of the primary inorganic particles. Included were photomicrographs showing the geometric form of many of these particles. The paper also described the method used in preparing the organic-free mineral constituents for that work and the current study.

The present paper presents information on surface area, pore structure, and pore volume of oil shale and its mineral constituents, and the manner in which the organic matter is distributed through the shale. Based on the surface area of the mineral constituents and some logical assumptions, the maximum amount of organic matter in contact with the surface of the inorganic matrix is calculated.

EXPERIMENTAL

Preparation of Oil-Shale Samples

Two samples of approximately 200 pounds each were prepared by compositing random samples of EF and B bed shales from the Bureau of Mines experimental oil-shale mine near Rifle, Colorado (13). The composite sample from EF bed assayed 28.6 gallons a ton and that from B bed 75 gallons a ton. These were crushed to pass a 2-mesh-per-inch screen. A representative sample from each of the crushed oil shales was reduced to pass a 0.375-inch screen and a representative portion of this reduced further to pass a 200-mesh screen. The particles smaller than 44 microns were removed using a screening and washing technique. The remaining particles, 44 to 77 microns, were used to determine surface area, micropore structure, and pore volume. This particle-size range was selected to obtain a representative sample of the initial shale within a 4 to 5 gram sample, limited by the size of the adsorption bulb; to expose any naturally existing micropore structure, and to eliminate the surfaces of the extremely fine particles created during crushing. The 44 to 77 micron particles represented 53.4 and 42.6 weight percent of the respective 28.6- and 75-gallon-per-ton shales ground to pass 200-mesh. Chemical analyses indicated that their organic-inorganic ratios were quite similar to those of the 200-mesh shales prior to removing the particles smaller than 44 microns.

Apparatus

The low-temperature adsorption apparatus and technique employed for this study were similar to those described by Emmett (4), Joyner (1), and Reis (11). The

Pyrex-glass adsorption apparatus, fabricated in this laboratory, consisted of an adsorption bulb, calibrated gas burettes, mercury manometer, McLeod gauge, nitrogen-vapor-pressure thermometer, high vacuum system capable of 10^{-6} mm. of Hg., purification trains for nitrogen and helium, and reservoirs for the purified gases. The purity of the two gases exceeded 99.9 mole percent as determined by mass spectrometer.

Procedure

Oil Shale, 44 to 77 Microns. A sample of known weight was packed tightly into the adsorption bulb and degassed at 220°F. for 72 to 96 hours to attain a constant pressure of 10^{-6} mm. Hg. This degassing temperature was selected to clean the shale's surfaces without significantly changing its chemical or physical structure. To determine the effect of degassing time, runs as short as 8 hours were made. After degassing, the dead-space volume within the adsorption bulb was measured with helium at the temperature of liquid nitrogen. Subsequently the helium was pumped from the adsorption bulb and the sample again degassed at 220°F. for 30 minutes before determining its adsorption isotherm.

A complete adsorption isotherm at the temperature of liquid nitrogen was obtained by measuring the quantity of nitrogen adsorbed at pressures from a few millimeters to the saturation pressure of the nitrogen. Adsorption equilibrium was reached rapidly below a relative pressure of 0.35. Fifteen minutes was allowed for equilibrium before each successive known volume of nitrogen was admitted into the adsorption bulb. Above 0.35, two hours were allowed for equilibrium to be attained. This appeared ample time for the heat of adsorption to dissipate and for equilibrium to be established. To determine if equilibrium had occurred, the time was extended to six hours at several different relative pressures. No significant differences were noted when compared with two hours time. After completing the adsorption isotherm, the data for the desorption isotherm were obtained by removing a known volume of nitrogen and allowing the system to come to equilibrium before removing the next known volume of nitrogen. This was continued until the relative pressure dropped to 0.2. Equal time was allowed for desorption at the different relative pressures as was allowed for adsorption. Several adsorption-desorption runs were made for each of the two shales using different representative samples for each run. The loss in weight, probably due to decarboxylation and loss of volatile organic matter, ranged from 0.20 to 0.34 weight percent of the samples charged to the adsorption bulb.

Inorganic Constituents. Previous work (14) indicated that a high percentage of the primary inorganic particles were smaller than 44 microns. The term "primary" refers to the initial size of the particles. To retain their initial size and to maintain representation of the initial shales, a composite sample consisting of several hundred pieces, 0.25 to 0.375 inch, was selected from each of the two shales crushed to pass a 0.375-inch screen. The organic matter was removed from these samples by a thermal treatment which did not exceed 750°F. (14), and then each organic-free shale residue was blended to give two uniform samples before their respective adsorption and desorption isotherms were determined.

New inorganic particles, mainly calcium sulfate, were formed when the organic matter was removed. Because the calcium sulfate could exist as extremely fine particles and hence have an appreciable surface area, it was leached from a portion of each residue. Adsorption isotherms were determined on the water-soluble-free residues to compare their surface areas with those of the initial residues. The leached material represented 1.7 and 8.4 weight percent of the initial residues from the 28.6- and 75-gallon-per-ton shales. Because the residue from the rich shale contained such a high percentage of water-soluble material, both its adsorption and desorption isotherms were determined.

A sample, 5 to 6 grams, from each of the residues was packed tightly into separate adsorption bulbs, degassed at 600°F. for 16 hours, and then the dead-space volume determined. The sample was again degassed at 600°F. under high vacuum for 30 minutes before determining the respective isotherms. The time allowed for equilibrium to be attained after each addition of nitrogen was 15 to 30 minutes for relative pressures below 0.35 and two to three hours for those above 0.35. In obtaining the desorption data, the reverse time intervals were used for desorption to attain equilibrium. In a number of instances, the time between addition or removal of nitrogen was increased to 10 hours in the relative pressure region above 0.75. Comparison of these data with those from the shorter periods indicated that two to three hours was ample time for either adsorption or desorption to occur at the higher relative pressures.

INTERPRETATION OF RESULTS

The experimental data can be expressed in graphic form as adsorption and desorption isotherms. These relate volume of nitrogen adsorbed or desorbed per gram of sample as a function of the relative pressure, P/P_o, where P is the measured pressure within the adsorption bulb and P_o is the liquefaction pressure of nitrogen. The adsorption-desorption isotherms of the two oil shales, the primary inorganic particles from each shale, and those from the rich shale free of water-soluble material are presented in Figures 1, 2, 3, 4, and 5.

As classified by Brunauer (2), all of the adsorption isotherms are of the sigmoid or S-shaped type, also referred to as Type II, with an asymptotic approach to the P_o line. They were interpreted according to the method of Brunauer, Emmett, and Teller (3) who showed that S-shaped adsorption isotherms can be plotted according to the equation:

$$\frac{P}{V(P_o - P)} = \frac{1}{VmC} + \frac{(C-1)P}{VmCP_o} \quad \text{where}$$

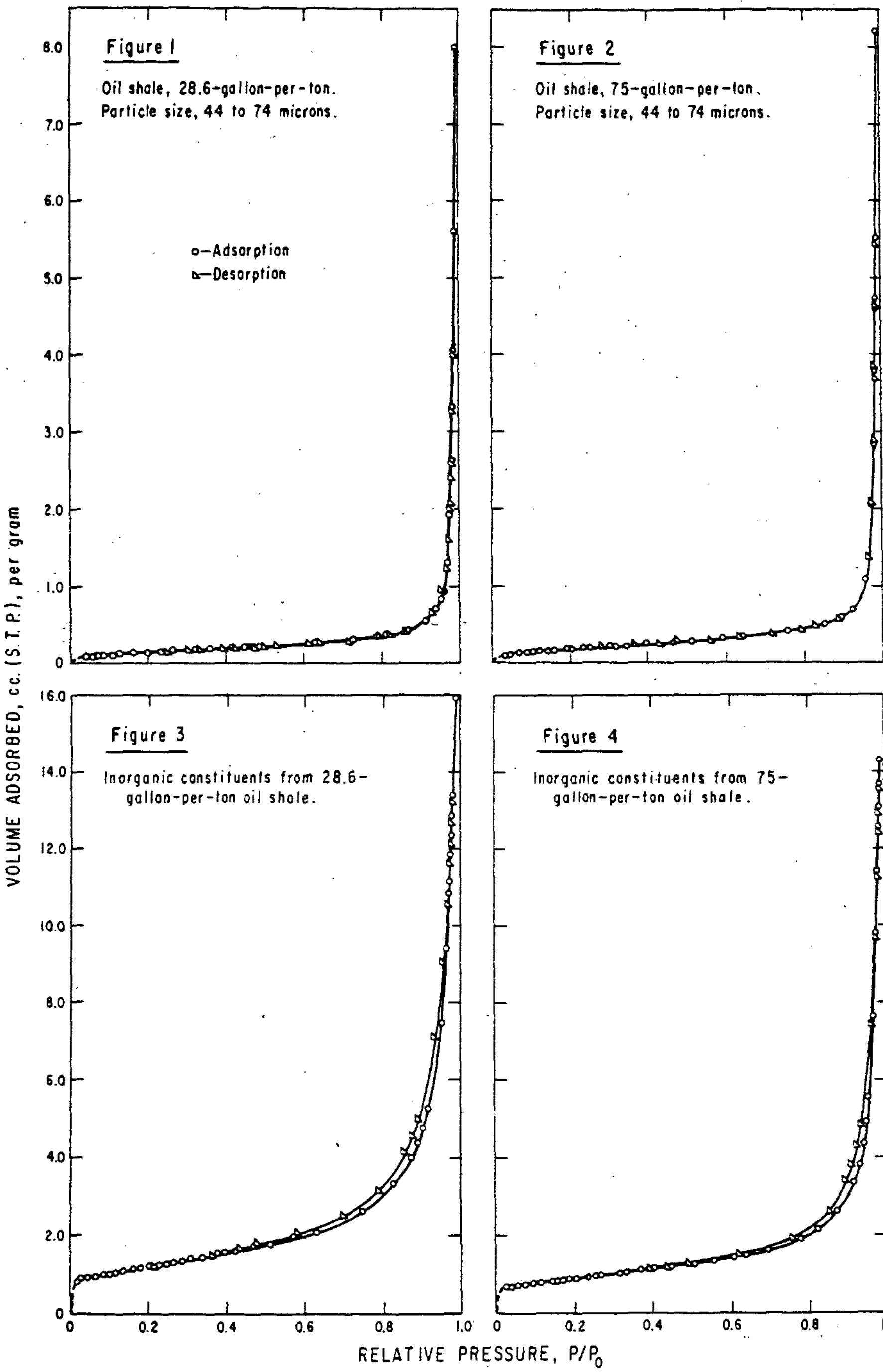
P = measured pressure
P_o = liquefaction pressure of the adsorbate
V = volume of gas adsorbed at pressure P
Vm = volume of gas required to form a monolayer
C = constant relating to heat of adsorption

A plot of $P/V\ (P_o - P)$ as a function of P/P_o is linear within the relative pressure range of 0.05 to about 0.35 provided the adsorption isotherm is of the sigmoid or S-shaped type. Deviations from linearity occur below and above this relative pressure range. They are negative up to 0.05 and positive above 0.35.

The experimental data for the two shales and the primary inorganic particles were plotted according to the BET equation and they are presented in Figures 6, 7, and 8. These adsorption isotherms are in excellent agreement with the BET theory. The volume of nitrogen, Vm., required to form a monolayer was calculated from the slope and intercept of these isotherms and then translated into area units, sq. meters per gram, using 16.2 A. (6) as the area of the adsorbed nitrogen molecule.

Oil Shale

Surface Area. The surface areas of the two shales are presented in Table I. That of the rich oil shale remained essentially constant with respect to degassing time while that from the leaner shale differed by about 0.14 sq. meter per gram. Why the surface area dropped was not known because the samples did not appear to be completely degassed before 96 hours. The values selected to represent the shale particles, 0.75 and 0.58 sq. meter per gram, were those after degassing for 96 hours. These values when converted to surface areas per cubic centimeter, were very close, 1.22 and 1.24 sq. meters per cc. respectively. They are about 20 times the surface area of nonporous spheres with a diameter midway between 44 to 74 microns when packed in a rectangular pattern and each successive layer resting in the depressions provided by the previous layer.



NITROGEN ADSORPTION-DESORPTION ISOTHERMS.

Table I. - Surface Area of Oil Shale, Particle Size, 44 to 74 Microns

Oil Shale	Weight, gms.	Degassing Temp., °F.	Degassing Time, hrs.	Vm cc./g.	Surface Area, Sq. M/g.	Surface Area, Sq. M/cc.
28.6 GPT1/	5.056	220	8	0.850	0.73	1.57
"	5.271	220	24	0.838	0.70	1.50
"	5.080	220	96	0.690	0.59	1.27
"	4.885	220	96	0.646	0.58	1.24
75 GPT	3.609	220	8	0.616	0.75	1.22
"	3.609	220	60	0.594	0.72	1.17
"	3.930	220	96	0.616	0.75	1.22

1/ Gallons per ton

Much of the surface area of the shale particles was probably contributed by surface roughness, induced fractures in the inorganic crystals exposed at the surfaces of these particles, and induced fractures in the organic matter itself brought about when the shale particles were prepared. Some of the surface area may be attributed to naturally occurring pores or capillaries with diameters less than 10 A. If such exist, their surface area could not be determined directly from the adsorption-desorption isotherms nor their presence detected, because within the relative pressure region, 0.05 to 0.35 capillary condensation presumably does not occur and hysteresis therefore would not be evident. The coverage of nitrogen on the adsorbate within this region varies from less than a monolayer up to about 1.5 monolayers (5). The small measured surface area of the shale particles indicates that surfaces attributed to capillaries or pores accessible through openings less than 10 A., if they occur, are not very large.

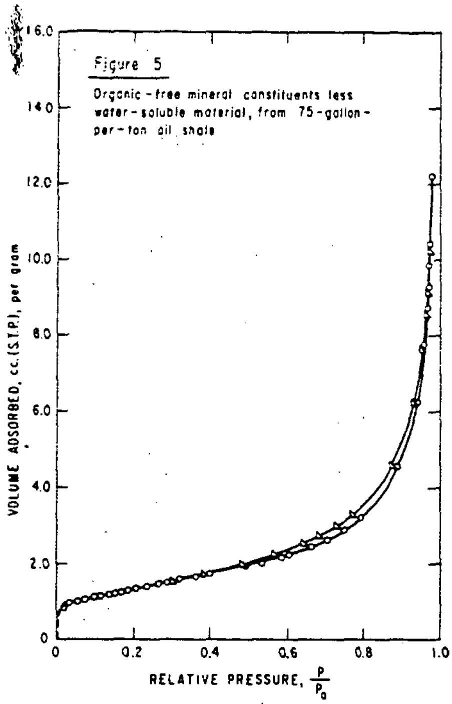
Pore Structure. Pore size, pore-size distribution, and pore volume of the adsorbent is obtained from adsorption-desorption isotherms and Kelvin's equation which relates the radius of a capillary to the relative pressure at which condensation takes place (11). Kelvin's equation is expressed as follows:

$$\ln \frac{P}{P_o} = \frac{-2\sigma V \cos\theta}{rRT}$$

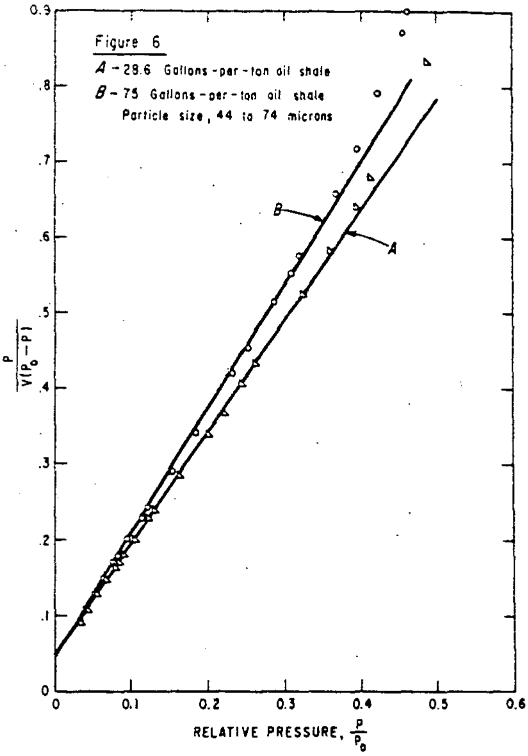
where

$\frac{P}{P_o}$ = relative pressure
r = capillary radius
σ = surface tension of the adsorbate
V = molar volume of liquid adsorbate
θ = angle of contact
R = gas constant
T = absolute temperature

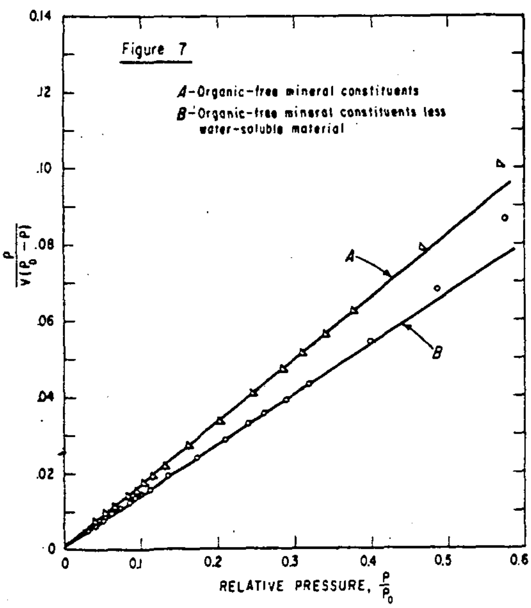
When capillary condensation occurs, the desorption isotherm usually lies well above the adsorption isotherm down to a relative pressure, near 0.4, which corresponds to the thickness of two monolayers of adsorbate. The nature of the pore structure determines the contour of the hysteresis loop in the desorption isotherm. Those which have hysteresis loops with plateaus followed by steep portions in the isotherm indicate a narrow pore-size distribution whereas curves free of inflection points indicate a broad pore-size distribution.

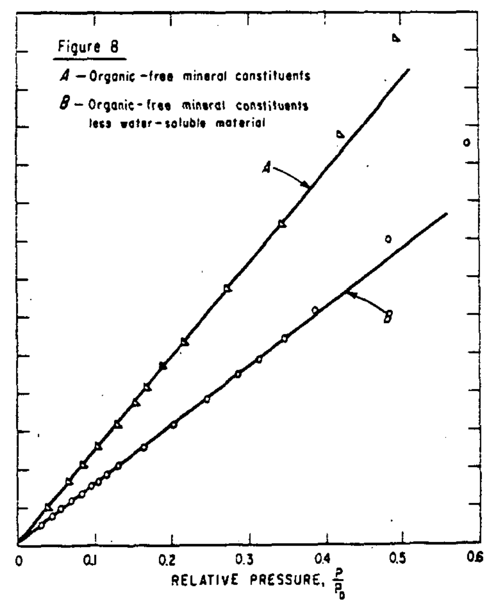


NITROGEN ADSORPTION-DESORPTION ISOTHERM.



NITROGEN ADSORPTION ISOTHERMS ACCORDING TO THE BET EQUATION.





NITROGEN ADSORPTION ISOTHERMS ACCORDING TO THE BET EQUATION.

The isotherms in Figures 1 and 2 show practically no hysteresis therefore little, if any, capillary condensation and evaporation. Deposition and removal of nitrogen apparently involved similar physical forces. This phenomenon indicates that the shale particles contained no appreciable amount of pores and/or capillaries with radii of the pore openings ranging from 10.5 to 235 A. as determined by Kelvin's equation.

Pore Volume. The pore volume can be calculated, from the quantity of nitrogen adsorbed between the relative pressure of 0.4 to 1.0. In Type II adsorption isotherms, however, which approach P_o asymptotically; the relative pressure at which capillary condensation is complete and interparticle condensation begins is not readily discernible. In Figures 1 and 2 the relative pressure selected for calculating pore volume was the intercept between the extrapolated near linear portions of each adsorption isotherm. In both isotherms the intercept occurred at 0.96. At this point all capillary condensation should be completed and all pores accessible through openings with radii up to 235 A. should be filled with liquid nitrogen. Reis (11) points out that there is reason to believe that in Type II isotherms, adsorption above a relative pressure of 0.90 may be interparticle condensation principally.

The pore volumes of the shale particles calculated from two different relative pressures, 0.96 and 0.90, are given in Table II. The value 0.808 was used as the density of nitrogen at the liquefaction pressure. As noted in Table II, the relative pressure selected to represent completion of capillary condensation significantly influences the calculated pore volume. The actual value may be somewhere between these two limits.

Table II. - Pore Volume of Oil-Shale Particles, 44 to 77 Microns

		Pore Volume			
		$\frac{P}{P_o} = 0.96$		$\frac{P}{P_o} = 0.90$	
Oil Shale	Weight, gms.	cc./gm.	Vol. %	cc./gm.	Vol. %
28.6 GPT	4.885	0.0013	0.28	0.0005	0.11
75 GPT	3.930	0.0013	0.21	0.0006	0.10

The pore volumes calculated from either relative pressure are small. These values, although small, may be higher than the true pore volume. Induced minute fractures in the shale particles as result of crushing and interparticle condensation probably contribute to these volumes. Because the isotherms in Figures 1 and 2 exhibit practically no hysteresis, they indicate absence of pore volume accessible through pore openings with radii smaller than 100 A.

Inorganic Constituents

Surface Area. The surface area of the primary inorganic particles free of organic matter and those free of both organic matter and water-soluble material were calculated from their respective BET plots, Figures 7 and 8, and presented in Table III. The particles free of water-soluble material had the higher value. This was not expected because of the calcium sulfates present. The increase in surface area over the initial inorganic particles may be attributed to separation of the platelet structure of some clay minerals, etching on the surface of minerals slightly soluble in water, removal of material other than calcium sulfate or a combination of these factors.

Pore Structure. In Figures 3, 4, and 5 the desorption isotherms exhibit hysteresis characteristic of porous materials yielding Type II isotherms. The hysteresis loops in

Table III. - Surface Area of Primary Inorganic Particles

Primary Inorganic Particles	Weight, gms.	Degassing Temp., °F.	Degassing Time, hrs.	Vm cc./g.	Surface Area Sq. M./g.
28.6 GPT Oil Shale 1/	6.261	600	16	0.969	4.24
75 " " 1/	6.915	600	16	1.081	4.73
28.6 " " 2/	5.711	600	16	0.713	3.12
75 " " 2/	6.323	600	16	1.029	4.15

1/ Initial
2/ Free of water-soluble material

the respective figures begin at relative pressures near 0.96, 0.97, 0.97 and all join the adsorption isotherms near 0.4. The smooth contours indicate that the pore openings in the primary inorganic particles have random pore-size distribution. Calculated from Kelvin's equation, the pore radii extend from 10.5 A. to 235 A. within the relative pressure region of 0.4 to 0.96 and 10.5 A. to 312 A. within 0.4 to 0.97. However, if condensation above a relative pressure of 0.90 is considered to be interparticle principally (11), the upper limit of the pore radii would be about 100 A.

Pore Volume. Pore volume per gram and percent porosity of the primary inorganic particles calculated from their respective isotherms, Figures 3, 4, and 5, are presented in Table IV. The volume occupied by the organic matter in 28.6- and 75-gallon-per-ton

Table IV. - Pore Volume of Primary Inorganic Particles

Primary Inorganic Particles	Weight, gms.	Pore Volume $\frac{P}{P_o}$ at 0.96 cc./g	Pore Volume $\frac{P}{P_o}$ at 0.96 Vol.%	Pore Volume $\frac{P}{P_o}$ at 0.90 cc./g.	Pore Volume $\frac{P}{P_o}$ at 0.90 Vol.%
28.6 GPT Oil Shale 1/	6.261	0.0096	2.66	0.0050	1.39
75 " " 1/	5.711	0.0086	2.36	0.0029	0.80
75 " " 2/	6.232	0.0079	2.16	0.0048	1.31

1/ Initial
2/ Free of water-soluble material

oil shales is 0.151 and 0.417 cc. per gram respectively. The maximum amount of the organic matter in the respective shales that could exist within the pores or capillaries of the primary inorganic particles is 6.36 and 2.06 volume percent based on the pore volumes obtained at a relative pressure of 0.96. The corresponding volume percents with respect to 0.90 relative pressure are 3.31 and 0.70. The pore volumes presented in Table IV show that the primary inorganic particles are not very porous and that the distribution of the organic matter in the shales appear to be essentially interparticle and not intraparticle.

Organic Matter in Contact with the Mineral Constituents.

Using surface area data and some logical assumptions an estimate can be made of the amount of organic matter in contact with the mineral constituents. The assumptions were: The organic molecules were spheres, 10 or 20 A. in diameter; the total surface of the mineral constituents was accessible for contact; and the spherical molecules formed a rectangular pattern on the surface. Based on the organic matter's density, 1.07, the approximate molecular weights of the 10 A. and 20 A. molecules would be 340 and 2700 respectively. The amount of organic matter represented by one monomolecular layer in contact with the surface is presented in Table V. This table also presents the number of monolayers the total organic could form if evenly distributed over the surface. These estimates suggest that only a small part of the organic matter is bonded either chemically or physically to the surface of the mineral constituents.

Table V. - Estimated Amount of Organic Matter in Contact with the Mineral Constituents

Mineral Constituents	Surface Area, Sq. M./g.	Dia. of Organic Molecule, A.	Organic Matter Represented by One Monolayer, Wt. %	No. of Monolayers from Total Organic Matter
28.6 GPT Oil Shale	4.24	10	3.11	32
" "	4.24	20	1.57	64
75 GPT "	3.12	10	0.57	175
" "	3.12	20	0.29	345

SUMMARY

Data from low-temperature nitrogen adsorption-desorption isotherms on Green River oil shale and its mineral constituents provide a better understanding of its basic physical structure. These data indicate that oil shale is a highly consolidated material with no significant micropore structure, pore volume, or internal surface. This type of physical structure is not favorable to surface dependent chemical or physical processes as it restricts reactive fragments or molecules to the interface. It appears that access to the interior must be preceded by removing, either chemically or physically, successive monolayers or molecules of organic or inorganic matter.

The primary inorganic particles contain pores and/or capillaries with random pore-size distribution. Their pore radii extend from 10.5 A. to 235 A. The pore volume accessible through these pore openings is about 0.01 cc. per gram and the amount of organic matter in the 28.6- and 75-gallon-per-ton oil shales that could exist within these pore spaces was calculated as 6.36 and 2.06 volume percent respectively. These values are considered as maximum volumes. If condensation above a relative pressure of 0.90 was interparticle condensation principally, the volume percents would be about one half. The data show that the distribution of the organic matter within the inorganic matrix is essentially interparticle and not intraparticle.

The primary inorganic particles contain no extensive micropore structure as evidenced by the surface area, about 4 sq. meters per gram. Estimates made from surface area values and logical assumptions suggest that only a small percentage of the organic matter is in direct contact with the surfaces of the mineral constituents.

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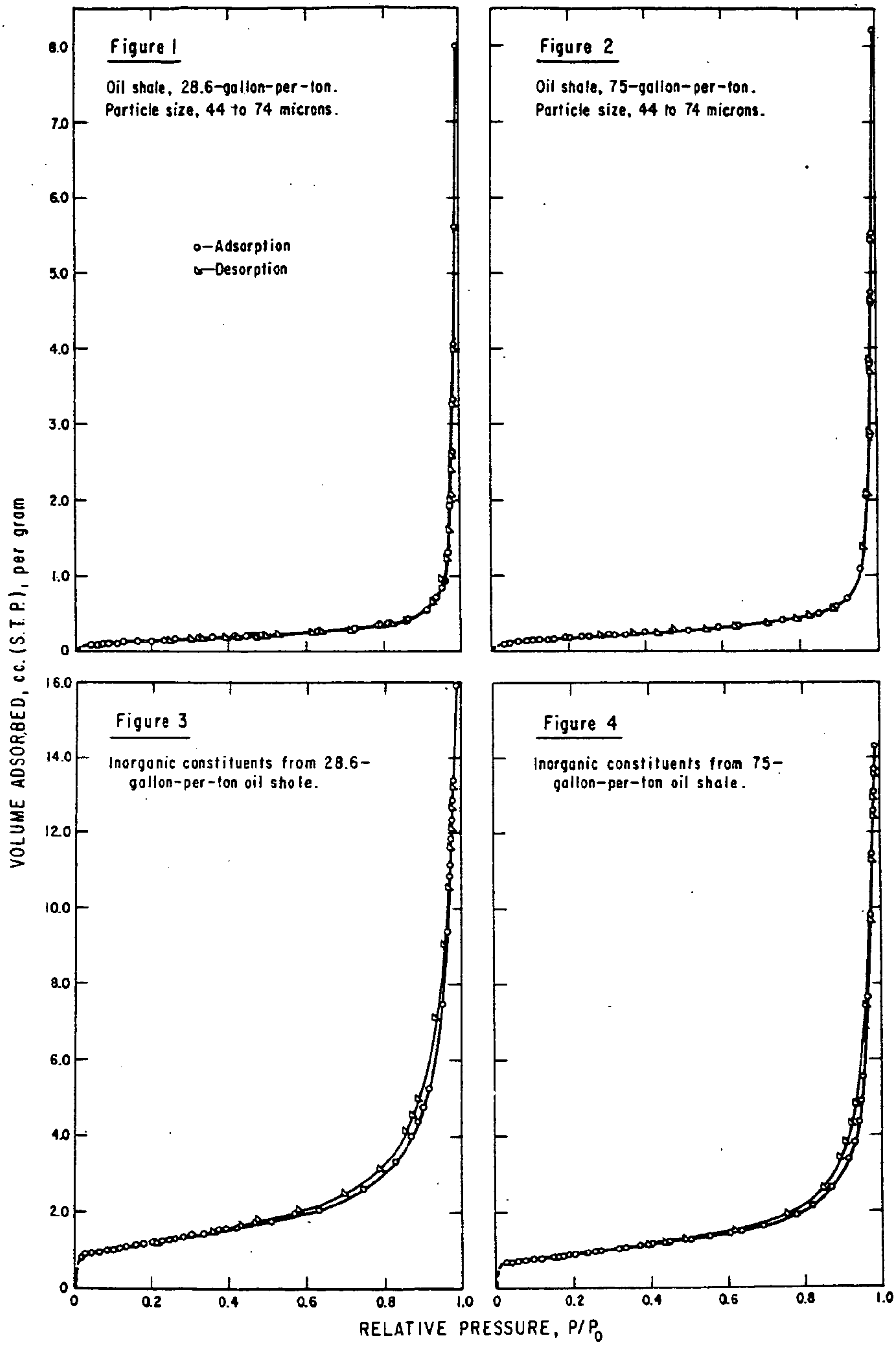

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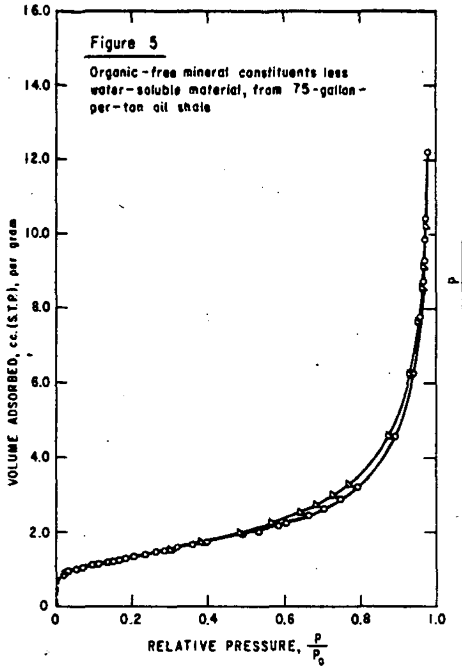

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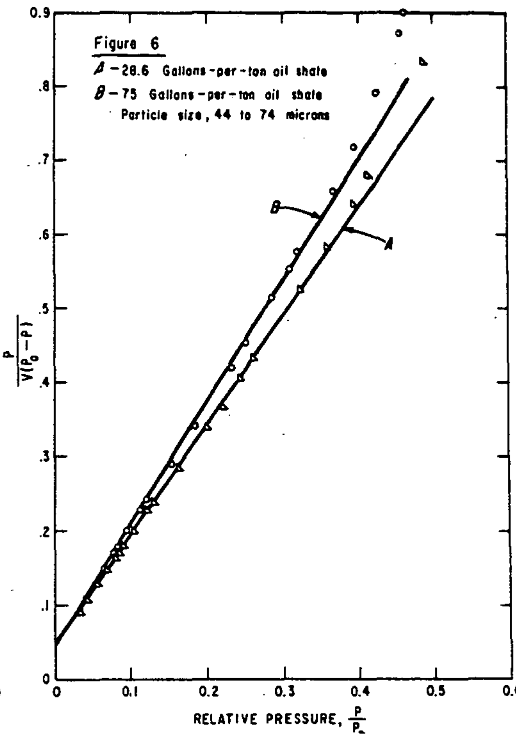

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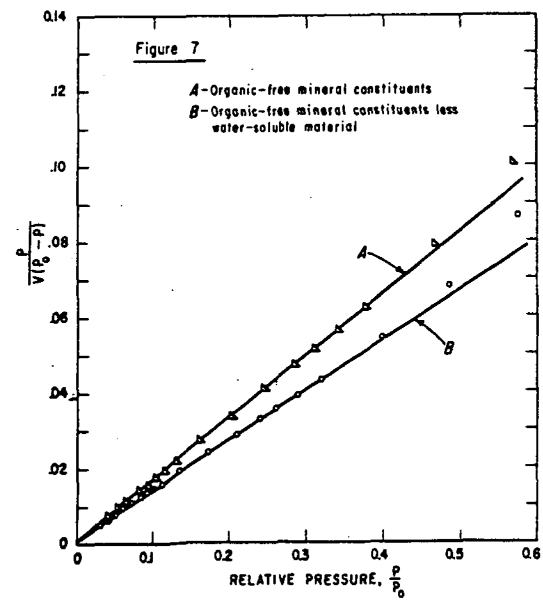

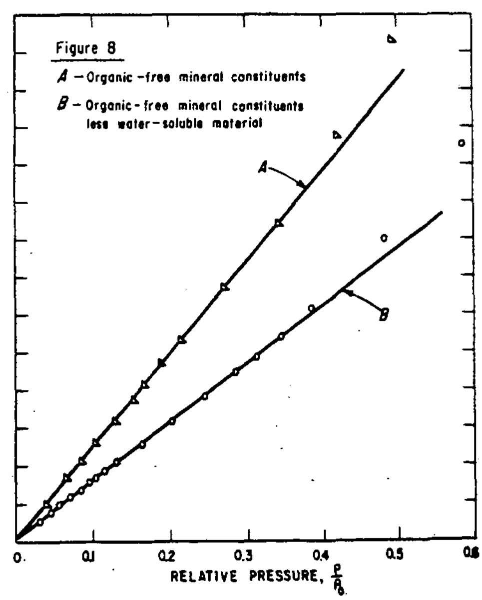

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